Supporting Information for: Heterobimetallic Complexes of Re and Zn: Potential Catalysts for Homogeneous Syngas Conversion

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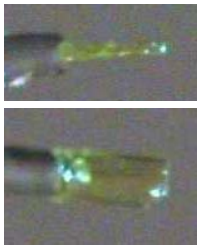
Table S1. Crystal data and structure refinement for 2 (CCDC 793163).

Empirical formula	$C_{25}H_{17}N_2O_3PBrRe \bullet C_6H_6$
Formula weight	768.59
Crystallization Solvent	Toluene/pentane
Crystal Habit	Plate
Crystal size	0.22 x 0.10 x 0.03 mm^3
Crystal color	Yellow



Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9916 reflections used in lattice determination	2.21 to 28.77°	
Unit cell dimensions	a = 14.7064(6) Å b = 10.7257(4) Å c = 18.0072(7) Å	α= 90° β= 92.959(2)° γ = 90°
Volume	2836.60(19) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.800 Mg/m^3	
F(000)	1488	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	1.74 to 30.56°	
Completeness to θ = 30.56°	99.1 %	
Index ranges	$-21 \le h \le 20$, $-14 \le k \le 15$, $-25 \le l \le 25$	
Data collection scan type	ω scans; 9 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	62872	
Independent reflections	8611 [R_{int}= 0.0553]	
Absorption coefficient	5.784 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8494 and 0.4335	

Table S1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8611 / 0 / 444
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.523
Final R indices [$I>2\sigma(I)$, 6973 reflections]	R1 = 0.0295, *w*R2 = 0.0426
R indices (all data)	R1 = 0.0452, *w*R2 = 0.0439
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.996 and -0.732 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S1. X-Ray Structure of 2.

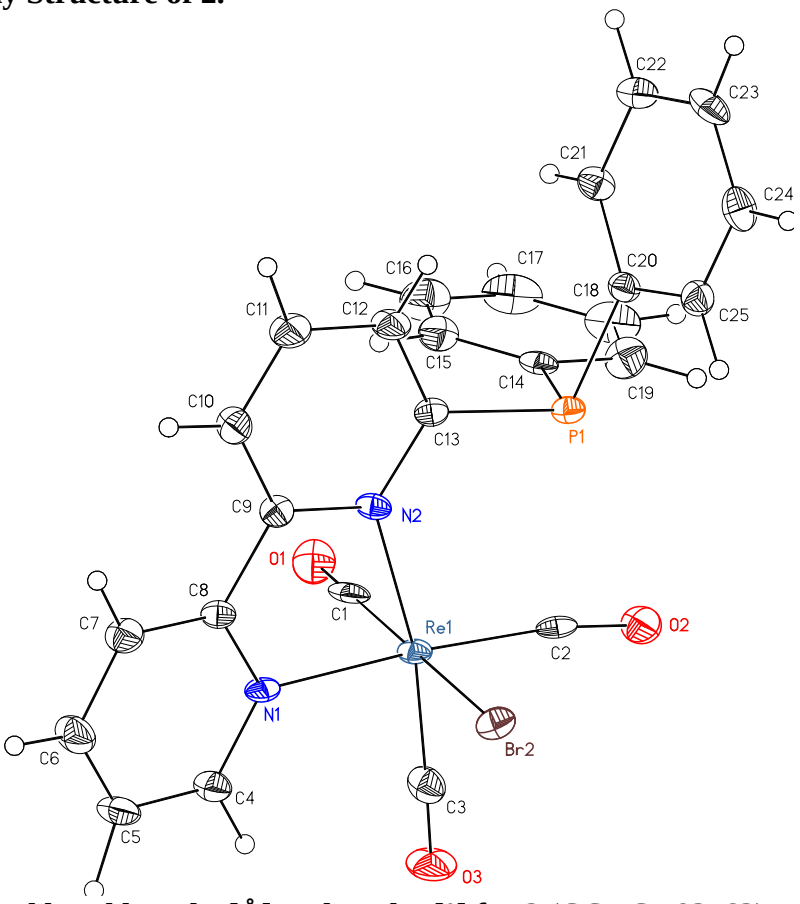


Table S2. Selected bond lengths [Å] and angles [°] for 2 (CCDC 793163).

Re(1)-C(3)	1.906(3)	C(3)-Re(1)-C(2)	83.14(13)
Re(1)-C(2)	1.927(3)	C(3)-Re(1)-C(1)	87.20(13)
Re(1)-C(1)	1.932(3)	C(2)-Re(1)-C(1)	90.75(12)
Re(1)-N(1)	2.165(2)	C(3)-Re(1)-N(1)	95.31(12)
Re(1)-N(2)	2.226(2)	C(2)-Re(1)-N(1)	174.43(10)
Re(1)-Br(2)	2.6075(3)	C(1)-Re(1)-N(1)	94.52(10)
		C(3)-Re(1)-N(2)	170.11(12)
		C(2)-Re(1)-N(2)	106.75(10)
		C(1)-Re(1)-N(2)	92.80(10)
		N(1)-Re(1)-N(2)	74.82(8)
		C(3)-Re(1)-Br(2)	95.57(10)
		C(2)-Re(1)-Br(2)	91.45(8)
		C(1)-Re(1)-Br(2)	176.65(9)
		N(1)-Re(1)-Br(2)	83.36(6)
		N(2)-Re(1)-Br(2)	84.15(5)

Table S3. Crystal data and structure refinement for 3 (CCDC 793162).

Empirical formula	$C_{26}H_{17}N_2O_4PBrRe$
Formula weight	718.50
Crystallization Solvent	Toluene/pentane
Crystal Habit	Block
Crystal size	0.20 x 0.16 x 0.12 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9810 reflections used in lattice determination	2.32 to 40.36°	
Unit cell dimensions	a = 11.2751(5) Å b = 14.2689(6) Å c = 30.2884(14) Å	α= 90° β= 98.082(2)° γ = 90°
Volume	4824.5(4) $Å^3$	
Z	8	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.978 Mg/m^3	
F(000)	2752	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	1.85 to 40.56°	
Completeness to θ = 40.56°	98.8 %	
Index ranges	$-20 \le h \le 20$, $-23 \le k \le 25$, $-55 \le l \le 55$	
Data collection scan type	ω scans; 14 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	220664	
Independent reflections	30593 [R_{int}= 0.0515]	
Absorption coefficient	6.797 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4723 and 0.3325	

Table S3 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	30593 / 0 / 631
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.326
Final R indices [$I>2\sigma(I)$, 22411 reflections]	R1 = 0.0309, *w*R2 = 0.0398
R indices (all data)	R1 = 0.0544, *w*R2 = 0.0422
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.005
Average shift/error	0.000
Largest diff. peak and hole	1.718 and -1.965 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S2. X-Ray Structure of 3

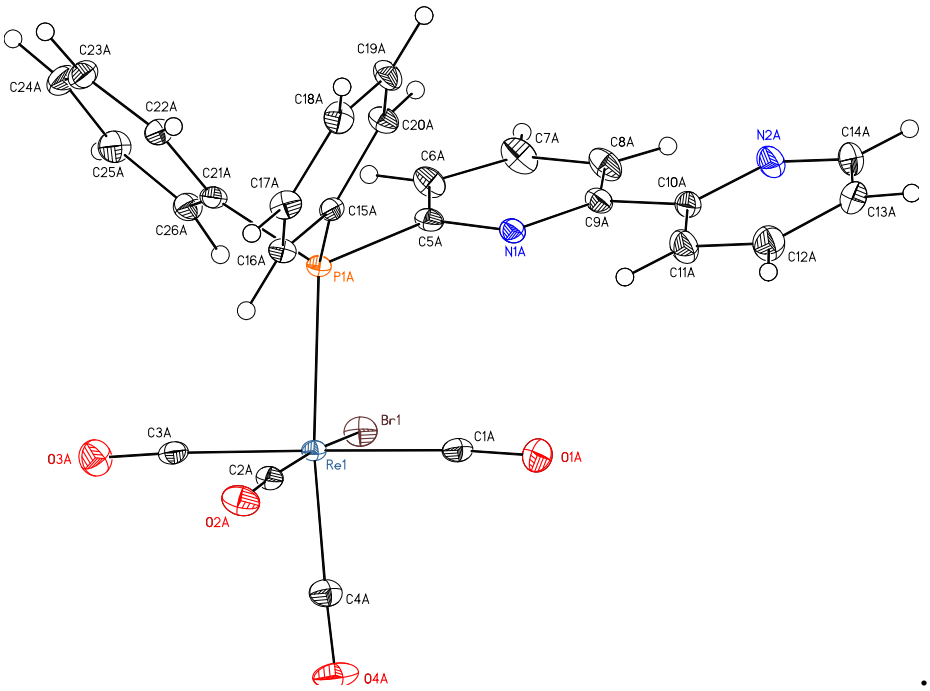


Table S4. Selected bond lengths [Å] and angles [°] for 3 (CCDC 793162).

Re(1)-C(2A)	1.9165(17)	Re(2)-C(2B)	1.9139(16)
Re(1)-C(4A)	1.9562(17)	Re(2)-C(4B)	1.9592(17)
Re(1)-C(3A)	2.0068(18)	Re(2)-C(1B)	2.0208(18)
Re(1)-C(1A)	2.0200(18)	Re(2)-C(3B)	2.0079(18)
Re(1)-P(1A)	2.4938(4)	Re(2)-P(1B)	2.4884(4)
Re(1)-Br(1)	2.62970(18)	Re(2)-Br(2)	2.62922(18)
C(2A)-Re(1)-C(4A)	89.71(7)	C(2B)-Re(2)-C(4B)	89.89(7)
C(2A)-Re(1)-C(3A)	90.87(7)	C(2B)-Re(2)-C(1B)	90.63(7)
C(4A)-Re(1)-C(3A)	90.24(7)	C(4B)-Re(2)-C(1B)	89.57(7)
C(2A)-Re(1)-C(1A)	91.49(7)	C(2B)-Re(2)-C(3B)	90.41(7)
C(4A)-Re(1)-C(1A)	88.56(7)	C(4B)-Re(2)-C(3B)	90.78(7)
C(3A)-Re(1)-C(1A)	177.35(6)	C(1B)-Re(2)-C(3B)	178.91(7)
C(2A)-Re(1)-P(1A)	98.44(5)	C(2B)-Re(2)-P(1B)	98.12(5)
C(4A)-Re(1)-P(1A)	170.99(5)	C(4B)-Re(2)-P(1B)	171.67(5)
C(3A)-Re(1)-P(1A)	93.45(5)	C(1B)-Re(2)-P(1B)	88.06(5)
C(1A)-Re(1)-P(1A)	87.41(5)	C(3B)-Re(2)-P(1B)	91.45(5)
C(2A)-Re(1)-Br(1)	172.83(5)	C(2B)-Re(2)-Br(2)	173.35(5)
C(4A)-Re(1)-Br(1)	84.86(5)	C(4B)-Re(2)-Br(2)	84.24(5)
C(3A)-Re(1)-Br(1)	84.49(4)	C(1B)-Re(2)-Br(2)	92.45(4)
C(1A)-Re(1)-Br(1)	93.04(5)	C(3B)-Re(2)-Br(2)	86.55(5)
P(1A)-Re(1)-Br(1)	87.313(10)	P(1B)-Re(2)-Br(2)	87.880(10)

Table S5. Crystal data and structure refinement for 8-Me (CCDC 757498).

Empirical formula	$C_{27}H_{20}Cl_2N_2O_4PReZn$
Formula weight	789.89
Crystallization Solvent	Dichloromethane/pentane
Crystal Habit	Needle
Crystal size	0.15 x 0.03 x 0.01 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9955 reflections used in lattice determination	2.36 to 31.74°	
Unit cell dimensions	a = 8.7910(5) Å b = 11.3904(7) Å c = 13.8593(8) Å	α= 81.394(4)° β= 79.674(4)° γ = 87.302(4)°
Volume	1349.63(14) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.944 Mg/m^3	
F(000)	764	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	1.81 to 32.04°	
Completeness to θ = 32.04°	99.0 %	
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 16$, $-20 \le l \le 20$	
Data collection scan type	ω scans; 15 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	39688	
Independent reflections	9287 [R_{int}= 0.0483]	
Absorption coefficient	5.663 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7463 and 0.6194	

Table S5 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	9287 / 0 / 423
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.343
Final R indices [$I>2\sigma(I)$, 7857 reflections]	R1 = 0.0280, *w*R2 = 0.0452
R indices (all data)	R1 = 0.0407, *w*R2 = 0.0466
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	2.021 and -1.327 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S3. X-Ray Structure of 8-Me.

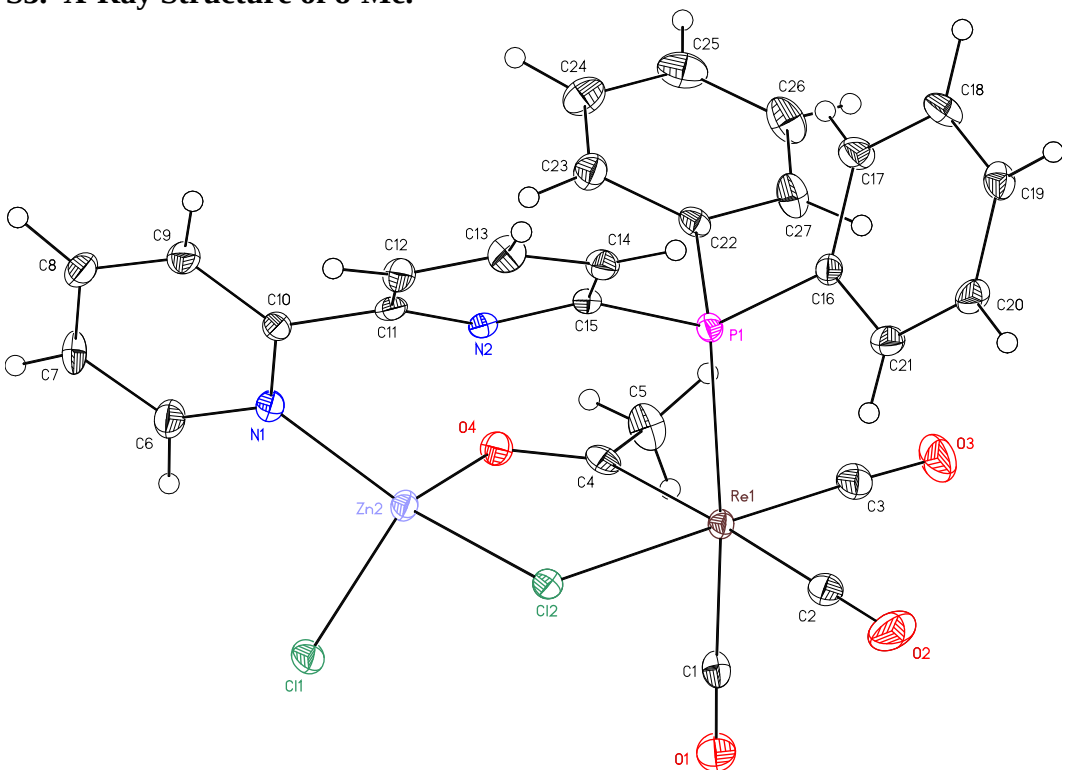


Table S6. Selected bond lengths [Å] and angles [°] for 8-Me (CCDC 757498).

Re(1)-C(3)	1.895(3)	C(3)-Re(1)-C(2)	87.05(12)
Re(1)-C(2)	1.963(3)	C(3)-Re(1)-C(1)	89.49(11)
Re(1)-C(1)	1.957(3)	C(2)-Re(1)-C(1)	91.45(11)
Re(1)-C(4)	2.185(3)	C(3)-Re(1)-C(4)	93.50(11)
Re(1)-P(1)	2.4641(7)	C(2)-Re(1)-C(4)	177.18(11)
Re(1)-Cl(2)	2.5406(6)	C(1)-Re(1)-C(4)	85.79(10)
Zn(2)-O(4)	1.9475(19)	C(3)-Re(1)-P(1)	89.40(8)
Zn(2)-N(1)	2.038(2)	C(2)-Re(1)-P(1)	98.08(8)
Zn(2)-Cl(1)	2.2678(7)	C(1)-Re(1)-P(1)	170.33(8)
Zn(2)-Cl(2)	2.3023(7)	C(4)-Re(1)-P(1)	84.69(7)
		C(3)-Re(1)-Cl(2)	177.69(9)
		C(2)-Re(1)-Cl(2)	90.65(8)
		C(1)-Re(1)-Cl(2)	90.79(8)
		C(4)-Re(1)-Cl(2)	88.81(7)
		P(1)-Re(1)-Cl(2)	90.71(2)
		O(4)-Zn(2)-N(1)	117.32(9)
		O(4)-Zn(2)-Cl(1)	103.61(6)
		N(1)-Zn(2)-Cl(1)	100.48(6)
		O(4)-Zn(2)-Cl(2)	99.78(6)
		N(1)-Zn(2)-Cl(2)	127.27(7)
		Cl(1)-Zn(2)-Cl(2)	105.83(3)
		Zn(2)-Cl(2)-Re(1)	98.96(2)

Table S7. Crystal data and structure refinement for 11 (CCDC 757305).

Empirical formula	$C_{26}H_{17}ClN_2O_4PReZn \bullet CH_2Cl_2$
Formula weight	824.33
Crystallization Solvent	Dichloromethane/hexanes
Crystal Habit	Fragment
Crystal size	0.19 x 0.15 x 0.14 mm^3
Crystal color	Orange

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9375 reflections used in lattice determination	2.44 to 46.42°	
Unit cell dimensions	a = 8.9302(4) Å b = 10.5871(4) Å c = 16.0479(6) Å	α= 96.985(2)° β= 94.550(2)° γ = 109.583(2)°
Volume	1407.13(10) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.946 Mg/m^3	
F(000)	796	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	2.07 to 48.39°	
Completeness to θ = 48.39°	97.5 %	
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 22$, $-33 \le l \le 33$	
Data collection scan type	ω scans; 27 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	119576	
Independent reflections	26771 [R_{int}= 0.0336]	
Absorption coefficient	5.528 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7495 and 0.6504	

Table S7 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	26771 / 0 / 428
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.470
Final R indices [$I>2\sigma(I)$, 22985 reflections]	R1 = 0.0265, *w*R2 = 0.0405
R indices (all data)	R1 = 0.0367, *w*R2 = 0.0413
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Largest diff. peak and hole	3.528 and -1.296 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S4. X-Ray Structure of 11.

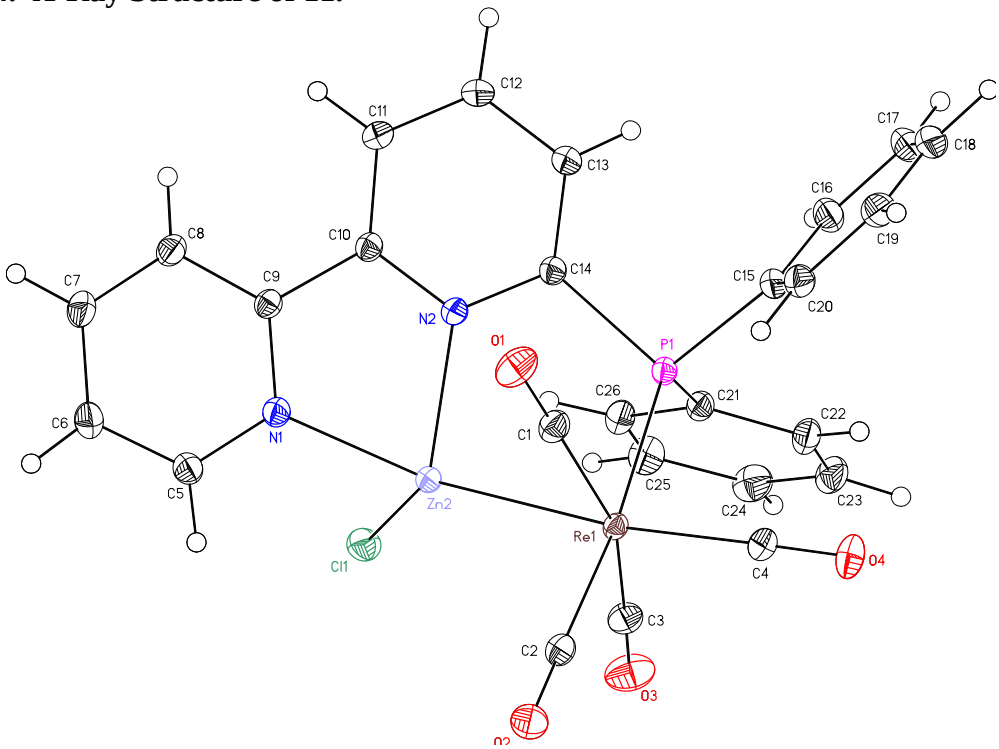


Table S8. Selected bond lengths [Å] and angles [°] for 11 (CCDC 757305).

Re(1)-C(4)	1.9368(9)	C(4)-Re(1)-C(2)	93.79(4)
Re(1)-C(2)	1.9642(10)	C(4)-Re(1)-C(1)	102.42(4)
Re(1)-C(1)	1.9704(10)	C(2)-Re(1)-C(1)	90.20(4)
Re(1)-C(3)	1.9700(11)	C(4)-Re(1)-C(3)	98.06(4)
Re(1)-P(1)	2.4273(3)	C(2)-Re(1)-C(3)	89.77(4)
Re(1)-Zn(2)	2.61977(15)	C(1)-Re(1)-C(3)	159.48(4)
Zn(2)-N(2)	2.1158(8)	C(4)-Re(1)-P(1)	92.20(3)
Zn(2)-N(1)	2.1259(8)	C(2)-Re(1)-P(1)	174.01(3)
Zn(2)-Cl(1)	2.3126(3)	C(1)-Re(1)-P(1)	88.38(3)
		C(3)-Re(1)-P(1)	89.52(3)
		C(4)-Re(1)-Zn(2)	171.49(3)
		C(2)-Re(1)-Zn(2)	94.68(3)
		C(1)-Re(1)-Zn(2)	78.35(3)
		C(3)-Re(1)-Zn(2)	81.20(3)
		P(1)-Re(1)-Zn(2)	79.333(6)
		N(2)-Zn(2)-N(1)	76.55(3)
		N(2)-Zn(2)-Cl(1)	109.13(2)
		N(1)-Zn(2)-Cl(1)	92.85(2)
		N(2)-Zn(2)-Re(1)	96.70(2)
		N(1)-Zn(2)-Re(1)	139.93(2)
		Cl(1)-Zn(2)-Re(1)	125.978(8)